

# Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing

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## Abstract

Phenolic compounds in wastewaters are difficult to treat using the conventional biological techniques such as activated sludge processes because of their bio-toxic and recalcitrant properties and the high volumes released from various chemical, pharmaceutical and other industries. In the current work, a modified heterogeneous advanced Fenton process (AFP) is presented as a novel methodology for the treatment of phenolic wastewater. The modified AFP, which is a combination of hydrodynamic cavitation generated using a liquid whistle reactor and the AFP is a promising technology for wastewaters containing high organic content. The presence of hydrodynamic cavitation in the treatment scheme intensifies the Fenton process by generation of additional free radicals. Also, the turbulence produced during the hydrodynamic cavitation process increases the mass transfer rates as well as providing better contact between the pseudo-catalyst surfaces and the reactants.

A multivariate design of experiments has been used to ascertain the influence of hydrogen peroxide dosage and iron catalyst loadings on the oxidation performance of the modified AFP. Higher TOC removal rates were achieved with increased concentrations of hydrogen peroxide. In contrast, the effect of catalyst loadings was less important on the TOC removal rate under conditions used in this work although there is an optimum value of this parameter. The concentration of iron species in the reaction solution was measured at 105 min and its relationship with the catalyst loadings and hydrogen peroxide level is presented.

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## 1. Introduction

Certain aromatic or phenolic compounds in wastewaters exhibit biotoxicity and recalcitrance to conventional biological oxidation process and consequently prove difficult to treat. With an increase in the stringent water quality regulations due to environmental concerns there is a huge demand for upgrading current water treatment technologies and the development of novel and more economical processes that can effectively deal with soluble toxic and non-biodegradable organic content in wastewater. Advanced oxidation technologies [1,2] have proven to be highly effective, though they have

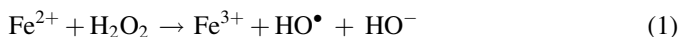
limitations of high investment cost for installation and operational costs due to the consumption of large amounts of energy/reagents in the process. These factors often limit the use of these alternative technologies even when cheaper processes are much less effective. Advanced oxidation processes (AOP's) are based on the formation of highly reactive hydroxyl radical species which act as an oxidant for the mineralisation of target compounds present in the aqueous solution. Among AOP's Fenton's reagent, which is a highly economical and effective treatment in terms of removing organic pollutants from industrial effluents, is one of the better chemical oxidation processes [3].

In a conventional Fenton process, iron salts in the presence of hydrogen peroxide under acidic milieu produce very highly reactive hydroxyl radicals (Eq. (1)) which then react with the

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pollutant to degrade the organic molecules present in the solution.



The use of zero-valent iron metal has been shown to be effective for the removal of toxic organic pollutants from water. In one sense, it is a cost effective treatment process which employs the direct use of metals and reduces the process cost by replacing metal salts. Zero-valent iron has been used for the degradation of azo dyes [4,5], phenol [6–8], chlorophenols [9] and nitro aromatic compounds [10]. In the AFP [8], zero-valent iron acts as a catalyst in place of ferrous salts. Initially, iron metal pieces produce ferrous ions and hydrogen gas when subjected to acid conditions (Eq. (2)). The ferrous ions then produce hydroxyl radicals in a similar way to the normal Fenton reaction (Eq. (1)). However, in the AFP the ferric iron is reduced to ferrous by interaction with zero valent iron (Eq. (3)) and the cycle continues as long as there is hydrogen peroxide present.



Hydrodynamic cavitation has been shown to be effective for the production of highly reactive free radicals due to the creation of high temperature and pressure and generation of intense turbulence and liquid circulation currents, which can be effectively harnessed for wastewater treatment applications [11–13]. Apart from a few reports [11,12] for synthetic effluents, use of hydrodynamic cavitation reactors in real industrial wastewater treatment applications has been rarely investigated possibly due to the lower intensity of cavitation generated in the reactors. The best approach for utilizing the impressive properties of hydrodynamic cavitation is to use it in combination with advanced oxidation processes and exploit the synergistic effects expected due to a common mechanism of destruction. The present work reports the use of hydrodynamic cavitation in combination with the advanced Fenton process. In continuation of our earlier work [6,14,15] dealing with establishing efficient treatment strategies for destruction of pollutants, phenol has been selected as a model pollutant. The outcome of different operating parameters on the extent of degradation has been established while the effectiveness of the treatment performance of the process described has been determined by monitoring the decrease of the total organic carbon (TOC) content in the solution at regular time intervals. Additionally, the amount of oxidant and catalyst, which produces the best results in terms of pollutant destruction has been optimized using multivariate analysis.

## 2. Materials and methods

### 2.1. Experimental set-up

Hydrodynamic cavitation was generated using a liquid whistle reactor (LWR) which is coupled to a positive

displacement pump and is employed in a comprehensive system containing the motor, base, variable frequency drives, pressure and flow measuring devices. The system consists of a feed vessel tank with a 5 L capacity, a plunger pump (Giant Industries, Model P220A, USA) with a power consumption of 3.6 kW and having a speed of 1750 rpm and a mixing chamber comprising of an orifice (orifice area,  $7.74 \times 10^{-7} \text{ m}^2$ ) and a blade (length, 0.0268 m; width, 0.0222 m; thickness, 0.0015 m). The pump has a maximum discharge pressure of up to 2000 psi (13,788 kPa). The distance between the orifice and blade is adjustable and the backpressure valve connected at the end of the mixing chamber influences the pressure. Aqueous phenol solution was circulated through the orifice chamber and subsequent iron chamber at a fixed flow rate of  $8.67 \times 10^{-5} \text{ m}^3/\text{s}$  for a desired contact time. A schematic representation of the intensified hydrodynamic cavitation generated by the LWR in conjunction with the AFP is shown in Fig. 1.

### 2.2. Experimental methodology

All experiments were carried out with 4 L of “synthetic” phenol wastewater for a period of 1–2 h reaction time with zero-valent iron pieces (unless specified otherwise, 80 g; 50 pieces of 1 cm × 2 cm, L-shaped having thickness of 0.10 cm) and  $\text{H}_2\text{O}_2$  (usually 2000 mg/L unless specified otherwise). Dilute solutions of sulphuric acid (2 M) and sodium hydroxide (2 M) were used for the adjustment of pH. The temperature was maintained constant at  $35 \pm 3^\circ \text{C}$  using an external cooling ice bath. At defined time intervals, samples were taken and analysed for TOC and total dissolved iron content present in the solution. The experimental runs were repeated 3 times to check the reproducibility of the data and the reported values are the average of these individual runs. The variation observed in the experimental data was in the range  $\pm 2\%$ .

The extent of mineralisation was determined by direct injection of the filtered samples into the heated persulphate-type ( $100^\circ \text{C}$ ) TOC analyser (Model 700, OI Analytical). The total dissolved iron content present in the solution after the reaction was measured by a calorimetric process in a DR/2000

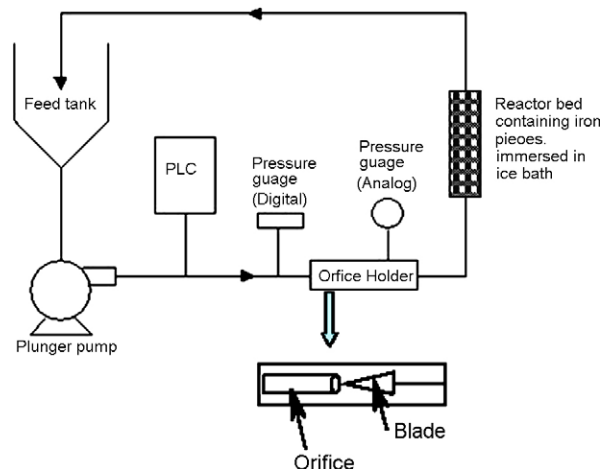


Fig. 1. Schematic representation of the experimental setup with expanded view of arrangement of orifice and blade.

Spectrophotometer (Hach) after proper dilution using the FerroVer Iron reagent. The FerroVer Iron reagent combines 1,10-phenanthroline with a reducing agent which converts any iron present into the +2 oxidation state ( $\text{Fe}^{2+}$ ). The 1,10-phenanthroline then reacts with  $\text{Fe}^{2+}$  to form an orange coloured complex, the intensity of which, measured at 510 nm, is directly proportional to the amount of  $\text{Fe}^{2+}$  present in the sample. The pH of the solution was determined using a Hanna pH meter.

### 3. Results and discussion

The current study evaluates the phenol degradation in a hydrodynamically enhanced advanced Fenton process. The various important operating parameters which affect the efficacy of the process include: operating pressure of the hydrodynamic cavitation reactor; location of the catalyst bed relative to the hydrodynamic cavitation reactor; initial phenol concentrations; and dosage of hydrogen peroxide. The effects of each of these operating parameters on the extent of TOC removal are discussed below.

#### 3.1. Effect of inlet pressure

Fig. 2 shows the extent of TOC mineralization obtained as a function of the operating pressure in the hydrodynamic cavitation reactor in the presence of a zero valent iron bed downstream of the orifice. Using our experimental set-up, it should be noted here that without the use of an iron catalyst bed, hydrodynamic cavitation alone resulted only in marginal reduction in the TOC. This indicates that presence of iron, acting as a pseudo catalyst, is a requirement for obtaining reasonable extents of phenol degradation or TOC removal. Fig. 2 also shows the extent of degradation obtained in the absence of the orifice and blade, i.e. without any hydrodynamic cavitation. It can be seen that about 40% reduction of TOC is obtained in 80 min of treatment time without the input of hydrodynamic cavitation and it only marginally increases at the 300 psi operating pressure. A substantial increase in the extent of TOC removal is however

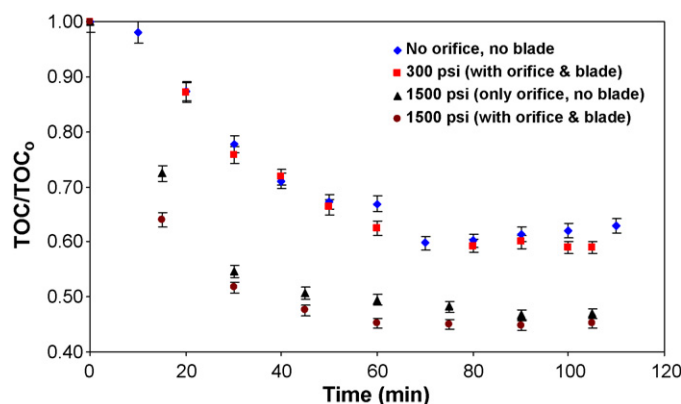


Fig. 2. Effect of inlet pressure in the hydrodynamic cavitation reactor on the TOC removal ratio. Experimental conditions: pH 2.5; phenol concentration 2.5 mM,  $\text{H}_2\text{O}_2$  2000 mg/L; iron 80 g (50 pieces of 1 cm  $\times$  2 cm, L-shaped having thickness of 0.10 cm); orifice area 0.012 in.<sup>2</sup>.

obtained when the inlet pressure is increased to 1500 psi (without the blade) where maximum contribution from hydrodynamic cavitation is expected. This required inlet pressure for the onset of cavitation effects is also dependent on the geometry of the cavitation chamber and it has been shown that with a proper optimization of the geometry of the setup, onset of cavitation can be obtained at inlet pressures as low as 15 psi [16]. The acceleration in degradation of organic contaminants with increasing pressure at 1500 psi (10,340 kPa) can be attributed to the enhancement of the hydroxyl radical production as a result of the intensification of cavitation activity. Bubble dynamics studies [17] have indicated that the cavitation intensity quantified in terms of the pressure pulse generated at the collapse of the cavity increases as a result of an increase in the inlet pressure of the system. It should be noted that the cavitation intensity is also dependent on the recovered pressure but in the present case the change in the recovered pressure was only marginal as compared to the change in the inlet pressure and hence the cavitation intensity is dominantly affected by the changes in the inlet pressure. Since there is elevated cavitation collapse intensity at higher inlet pressures, a higher temperature and pressure pulse is generated resulting in enhanced dissociation of the water molecules trapped in the cavity thereby leading to more hydroxyl radicals.

Use of a blade just adjacent to the orifice, at same operating pressure, results in further, but minimal, increase in the extent of TOC removal observed in the reactor. This increase can be attributed to the fact that the system acts as multiple orifices resulting in a greater number of cavitation events and hence the overall cavitation intensity is greater resulting in enhanced degradation. Superior degradation with higher inlet pressures and multiple orifices is consistent with other literature reports. Vichare et al. [16] and Sivakumar and Pandit [11] have shown that an increase in the upstream pressure and use of multiple orifices on the plate raises the extent of oxidation of potassium iodide and degradation of rhodamine B, respectively.

To maximize the amount of degradation of the effluent stream in the present case, all further experiments were performed at an operating pressure of 1500 psi (10,340 kPa) with both orifice and blade in place. It should also be noted here that applying 1500 psi (10,340 kPa) may not be feasible on an industrial scale of operation where a modification in the design of the hydrodynamic cavitation unit (use of multiple orifice plates where the number of holes can be as high as 30–50) is recommended to get similar effects at much lower inlet pressures. The work of Vichare et al. [16] is recommended in order to get a greater insight into optimization of hydrodynamic cavitation reactors.

#### 3.2. Effect of catalyst bed location in the experimental set-up

Hydrodynamic cavitation and the Fenton oxidation process using iron as catalyst operates in a sequential manner as described above. Thus the location of the iron bed should also play an important role in the extent of observed synergistic effects. It is expected that the catalyst bed should be subjected

to the influence of cavities generated downstream of the orifice to get maximum benefits. The acceleration/enhancement in the process performance with respect to the catalyst bed location is due to the continuous cleaning of the active catalyst surface by the impingement of the liquid jet stream with high force at the iron metal surface and also by the collapsing microbubbles at the reactive sites on the surface generated by the hydrodynamic cavitation. The flow rate of the solution through the iron metal surface can thus significantly enhance the treatment performance through changing the contact time. Keeping this in mind, the effect of catalyst bed location (two positions; 23 and 50 cm from the orifice) on the TOC removal rates has been investigated. Experiments were carried out at each location with 4 L of phenol wastewater (initial concentration 2.5 mM), pH adjusted to 2.5, initial  $\text{H}_2\text{O}_2$  concentration of 2000 mg/L, initial pressure of 1500 psi and 50 iron metal pieces as catalyst in the modified AFP. Each experiment with the catalyst bed located close and far from the orifice was carried out in triplicate and the reported TOC values are the average values (the observed variation in each set was within  $\pm 2\%$ ). It has been observed that the extent of TOC mineralisation was marginally higher (however not within the limits of the experimental errors for these experimental runs) when the catalyst bed was located near the orifice (57%) as compared to that observed at a location away from the orifice (53%). Similar results were obtained with measurements of the total dissolved iron content (concentration was 252 mg/L for near location and 243 mg/L for location away from the orifice). The results indicate that the operating conditions in the present work are such that the intensity of hydrodynamic cavitation generated in the system is sufficient (due to very high inlet pressures into the cavitation chamber, it is expected that the cavitation intensity will be high) to maintain the active cavitation zone over a distance of 50 cm away from the point of generation (orifice) and only a marginal decay in the intensity of cavitation is observed as indicated by a decrease in the TOC removal rates. Still, the location of the catalyst bed in the system is an important design parameter especially in the case of large scale industrial wastewater treatment plants where higher distances are expected and where low operating pressures are used (a proper design of the experimental setup also allows generation of cavitation activity at much lower operating pressures and hence much lower operating costs). More work is indeed required on a larger scale of operation and with varying designs of cavitation chamber for generation of different cavitation intensities for optimisation of the relative location of the catalyst bed and orifice.

### 3.3. Effect of initial phenol concentration

The effect of initial phenol concentration on the TOC content has been investigated in the range of 0.5–1.5 mM at a pH 2.5,  $\text{H}_2\text{O}_2$  concentration of 2000 mg/L and at a pressure of 1500 psi with the modified AFP. Fig. 3 shows the corresponding mineralisation ratios obtained at different initial concentrations of phenol wastewater using iron metal pieces acting as a pseudo catalyst. In the first 10 min of the reaction, the solution turned

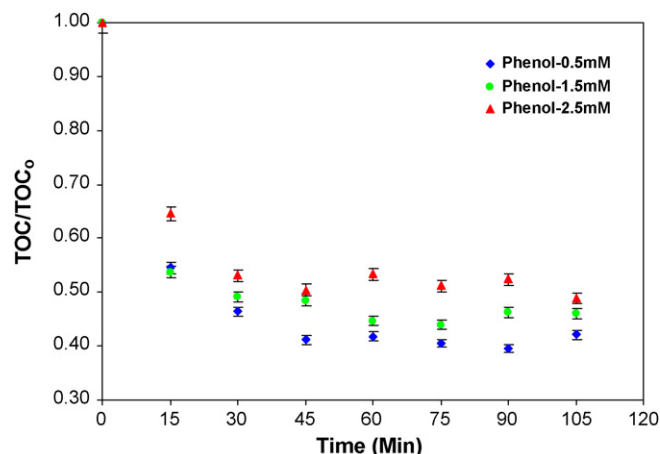


Fig. 3. Effect of initial phenol concentration on the TOC removal ratio using the modified AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM,  $\text{H}_2\text{O}_2$  2000 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm  $\times$  2 cm, L-shaped having thickness of 0.10 cm); orifice area 0.012 in.<sup>2</sup>.

brown in colour, which can be attributed to the formation of quinones and the solution got progressively darker within the next 5 min, indicating an accumulation of quinones or iron complexes. Further treatment for 10 min changed the dark solution to colourless. The pH of the solution remained constant throughout the experiment. It is evident from Fig. 3 that maximum TOC removal was obtained at a low phenol concentration of 0.5 mM (approximately 58%) and the TOC removal marginally decreased with an increase in the phenol concentration. The extent of TOC removal in 105 min of treatment time was 54% and 51% for the initial phenol concentrations of 1.5 and 2.5 mM, respectively. The observed results are consistent with the literature reports indicating better efficacy of both Fenton chemistry as well as cavitation phenomena at lower pollutant concentration [18–21]. It should be also noted here that the actual number of moles of phenol degraded are higher at 2.5 mM concentration as compared to 1.5 mM initial concentration. This also means that the extent of corrosion of the zero valent iron pieces and hence the extent of dissolved iron appearing into the solution increases. The observed results are consistent with our earlier observations with phenol degradation using the individual operation of advanced Fenton process [6].

### 3.4. Variation of total iron content concentration

The iron content in the solution also increased with longer treatment time due to continuous leaching during the flow and also with operating pressure and initial concentration of phenol. The trends in variation of the iron content of the stream with the treatment time and initial concentration of phenol are shown in Fig. 4. It can be seen that a maximum value of about 330 mg/L of iron in solution was observed for 90 min of treatment time at initial phenol concentration of 2.5 mM. An increase in the treatment time or initial phenol concentration shows higher amounts of degradation of phenol and results in the dissolution of more iron. These results are in good agreement with our earlier studies [6,8] and the detailed discussion into the chemistry



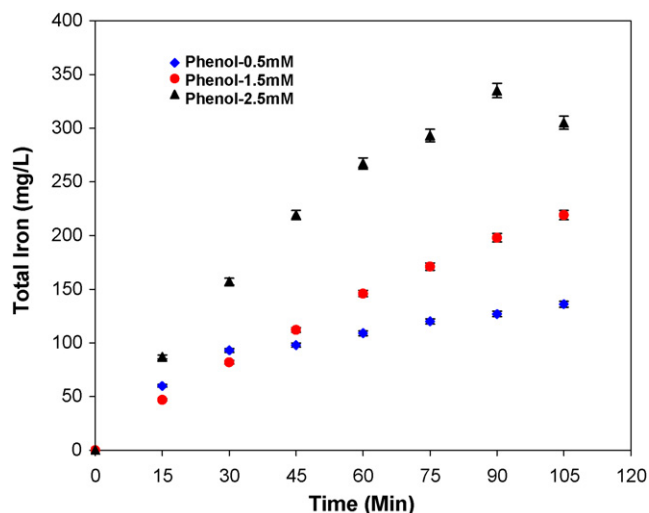


Fig. 4. Variation of total iron content of solution with treatment time and initial phenol concentration. Experimental conditions: pH 2.5; phenol concentration 2.5 mM,  $\text{H}_2\text{O}_2$  2000 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm  $\times$  2 cm, L-shaped having thickness of 0.10 cm); orifice area 0.012 in.<sup>2</sup>.

aspects of the advanced Fenton process can be referred to in our earlier work [6]. It should also be noted that the dissolved iron could easily be removed using a coagulation technique and hence does not represent any additional problem in terms of wastewater treatment. The outlet samples after treatment contained less than 10 mg/L iron following the coagulation treatment.

### 3.5. Effect of hydrogen peroxide concentration

The concentration of hydrogen peroxide plays a crucial role in determining the overall efficacy of the degradation process especially for Fenton chemistry. Usually the loading of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized in the process as the residual hydrogen peroxide contributes to COD and also is harmful to micro-organisms (important if the technique is used as a pre-treatment strategy for conventional aerobic oxidation). The effect of hydrogen peroxide concentration is shown in Fig. 5 and it can be clearly seen that the extent of degradation increases with the hydrogen peroxide concentration over the range 500–2000 mg/L. The observed trend is again consistent with the literature reports [22,23]. It has been established that the extent of increase in the TOC removal does not decrease with an increasing hydrogen peroxide concentration over the range investigated in the present work. An optimum hydrogen peroxide ratio must be selected as beyond a certain concentration, any excess might act as a scavenger for hydroxyl radicals and also contribute to excess COD in the pollutant stream. Thus, proper selection of the operating concentration of the oxidant is necessary and multivariate analysis (discussed below) provides some guidelines on the selection of the optimum operating parameters.

### 3.6. Factorial design of experiments for the modified AFP

The use of a multivariate design of experiments has proven to be an important tool for obtaining valuable and statistically

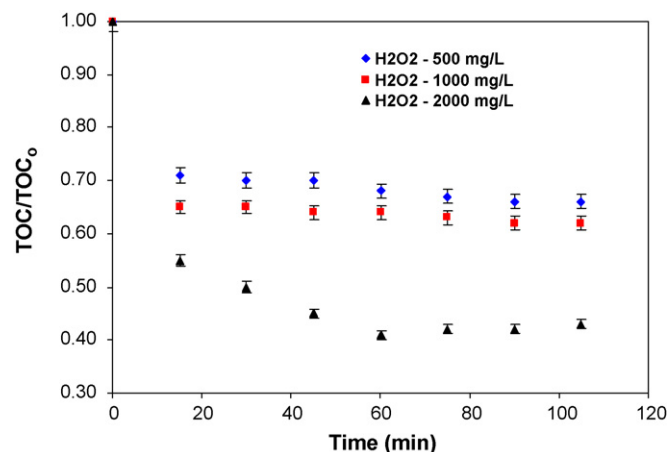


Fig. 5. Effect of hydrogen peroxide concentration on the TOC removal ratio using the modified AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM,  $\text{H}_2\text{O}_2$  2000 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm  $\times$  2 cm, L-shaped having thickness of 0.10 cm); orifice area 0.012 in.<sup>2</sup>.

significant models of phenomena by performing a well planned set of experiments. Using this technique, it is possible to assess the importance of each individual variable and the interaction effects between them, thereby yielding the most desirable response. Application of this statistical technique has been reported for the treatment of pollutants by photocatalytic oxidation [24] and the Fenton/sono-Fenton technique [14,23]. We now discuss the use of multivariate design of experiments to evaluate the importance of iron metal catalyst used in the combination of hydrodynamic cavitation and advanced AFP, and the hydrogen peroxide dosage in the TOC removal of phenol wastewater.

The influence of different variables in the modified advanced Fenton process was investigated using an experimental design methodology. The variables studied with this method include hydrogen peroxide dosage and different amounts of zero valent iron metal pieces acting as catalyst in our process. A complete  $3^2$  experimental design [25,26] was performed and employed different amounts of iron (25, 50 and 100 pieces, corresponding to low, medium and high amounts) and hydrogen peroxide (500, 1000 and 2000 mg/L, representing the low, medium and high amounts, respectively). The results for all the 9 experimental runs are presented for both experimental and calculated values in Table 1. The initial pH was adjusted to 2.5, by the addition of appropriate amounts of  $\text{H}_2\text{SO}_4$  solution (0.1 M). The objective was to minimize the hydrogen peroxide concentration in the process that accompanied high efficiency of degradation of phenol and the organic by-products formed in the reaction.

Table 1 shows the factorial design of the experiment, along with the real values for the independent variables (−1, 0 and 1 for low, medium and high levels, respectively). The response variables selected were TOC conversion at 15, 60 and 105 min of treatment time, with the objective of studying the influence of the independent variables on the activity and the amount of iron dissolved from the catalyst during the process, to determine the influence of the independent variables on the modified AFP. The values of these variables, as well as the

Table 1  
Factorial design of experiments

[Catalyst] (X)	[H <sub>2</sub> O <sub>2</sub> ] (Y)	X <sub>TOC</sub> <sup>15'</sup> (%) (Z <sub>1</sub> )		X <sub>TOC</sub> <sup>60'</sup> (%) (Z <sub>2</sub> )		X <sub>TOC</sub> <sup>105'</sup> (%) (Z <sub>3</sub> )		Fe <sub>Total</sub> <sup>105'</sup> (mg/L) (Z <sub>4</sub> )	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
–1	–1	25	25.1	29	29.6	30	30.7	370	365.9
–1	0	30	29.7	32	30.6	38	36.2	310	316.9
–1	1	40	40.2	45	46.0	50	51.2	250	247.2
0	–1	29	28.6	32	30.6	34	32.4	500	511.1
0	0	35	35.8	36	39.1	38	41.6	406	388.0
0	1	45	44.5	59	56.5	60	57.2	219	223.8
1	–1	30	30.2	33	33.7	35	35.8	536	530.1
1	0	40	40.0	42	40.2	45	42.9	425	434.4
1	1	46	46.3	49	50.1	52	53.2	280	276.9

calculated values obtained from the model are also shown in Table 1. The experimental values can be used to construct a matrix and assuming a second order polynomial model and a Levenberg–Marquand algorithm for nonlinear regression, predictive equations for the response variables were obtained (Eqs. (4)–(7) in Table 2), where *X* and *Y* represent the catalyst and hydrogen peroxide concentration, respectively, and *Z*<sub>1</sub> to *Z*<sub>3</sub> correspond to TOC conversion at 15, 60 and 105 min, respectively, and *Z*<sub>4</sub> the total iron dissolved after 105 min treatment time. The influence of the independent variables and their combination is related to the value and sign of the coefficients of the polynomial expressions. Values in parenthesis describe the relative error of each coefficient. Based on the experimental values, Origin software (version 6.1) was used to predict the equations that quantitatively describe each variable and to build the surface response curves.

### 3.7. Influence of process variables on the performance of the modified AFP

The conversion of TOC values at 15, 60 and 105 min was selected for the study of the performance of the novel heterogeneous system in the mineralization of the aqueous phenol solution. Eqs. (4)–(7) (Table 2) fit the experimental data obtained and it has been observed that the predicted values of the extent of degradation using these equations perfectly match the experimentally observed values. Considering the influence of the variables with the coefficients of the equations shown above, it is notable that the presence of quadratic terms in all the equations and the responses are graphically represented by the surface response curves. The amount of catalyst (*X*) is

important in all the reaction times, although a negative effect of an excess of catalyst (*X*<sup>2</sup>) becomes important with the reaction time. An excess of hydrogen peroxide (*Y*<sup>2</sup>) has a positive effect also and the synergistic effect of the catalyst (*X*) and hydrogen peroxide (*Y*<sup>2</sup>) becomes important at the reaction time of 105 min.

The graphical representation of the surface response curves of TOC removal for 15, 60 and 105 min is depicted in Fig. 6. The three surfaces are in the same shades of grey to make a comparison between them easy. The 3D-response surface at 15 min (Fig. 6a) clearly shows no significant increase in the TOC conversion with increasing catalyst loadings. Similar results were observed with the 3D response surface plots at 60 min (Fig. 6b) and at 105 min (Fig. 6c). Importantly, the maximum TOC conversion was obtained for elevated concentrations of hydrogen peroxide. The 3D response surface at 105 min clearly shows an enhanced TOC conversion with increasing concentration of hydrogen peroxide and this beneficial effect of hydrogen peroxide concentration on the TOC removal rates is also seen for the other two time intervals investigated in the present work as shown in Fig. 6a and b. This implies that the higher the amount of hydrogen peroxide (over the range selected in the present work) in conjunction with continuous generation of iron species in the reaction solution can produce more oxidising species, such as hydroxyl radicals, which can mineralise phenol solution. The same inference can also be obtained from the values of coefficients for each of these operating variables. From Eq. (6), it is clearly seen that the principal influence corresponds to hydrogen peroxide concentration (*Y*). It is seen that other variables such as *X*, *XY*, *X*<sup>2</sup>, *Y*<sup>2</sup> and the combination of catalyst pieces and hydrogen peroxide

Table 2  
Predicted equations obtained by factorial design of experiments

$$Z_1 = 35.8(\pm 0.9) + 4.95(\pm 0.8)X + 7.9(\pm 0.8)Y + 0.3(\pm 0.6)XY - 1.2(\pm 0.8)X^2 + 0.83(\pm 0.8)Y^2 - 0.1(\pm 1.0)X^2Y - 2.2(\pm 1.0)XY^2 \quad (4)$$

$$Z_2 = 39.1(\pm 3.7) + 4.8(\pm 3.5)X + 12.9(\pm 3.8)Y + 1.1E - 10(\pm 2.5)XY - 3.7(\pm 3.6)X^2 + 4.4(\pm 3.5)Y^2 - 4.7(\pm 4.5)X^2Y - 2.7(\pm 4.3)XY^2 \quad (5)$$

$$Z_3 = 41.6(\pm 4.3) + 3.3(\pm 4.1)X + 12.4(\pm 4.4)Y - 0.8(\pm 2.9)XY - 2.0(\pm 4.2)X^2 + 3.1(\pm 4.1)Y^2 - 2.9(\pm 5.2)X^2Y - 1.5(\pm 5.0)XY^2 \quad (6)$$

$$Z_4 = 388.0(\pm 18.9) + 58.8(\pm 17.5)X - 143.6(\pm 17.0)Y - 33.6(\pm 12.3)XY - 12.4(\pm 17.6)X^2 - 20.6(\pm 17.7)Y^2 + 50.6(\pm 20.8)X^2Y - 10.3(\pm 21.4)XY^2 \quad (7)$$

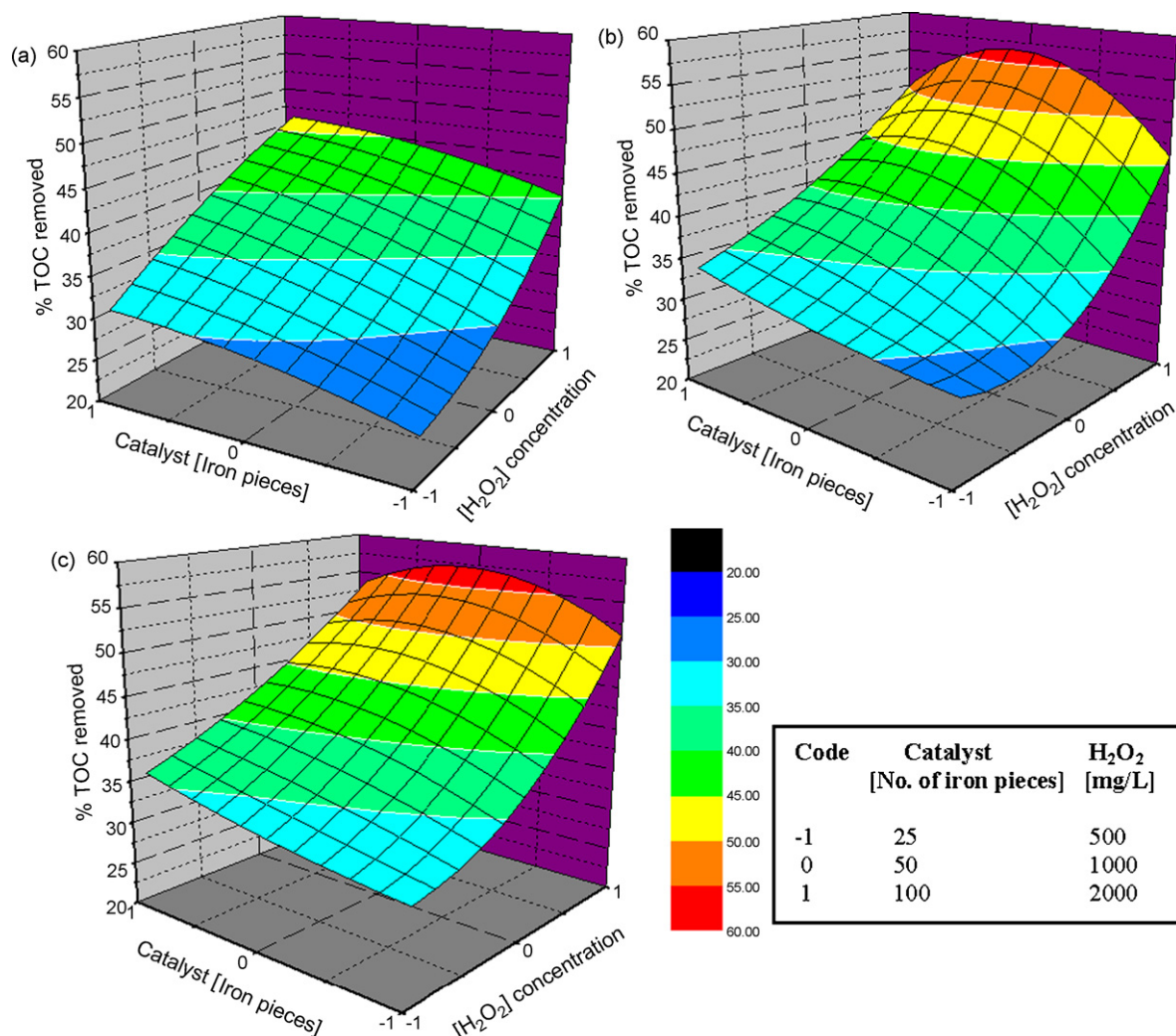


Fig. 6. Response surfaces for TOC conversion of phenol wastewater by the modified advanced Fenton process at (a) 15 min, (b) 60 min and (c) 105 min.

concentration ( $XY^2$  and  $X^2Y$ ) has less effect on the TOC removal rates since the relative error is bigger than the coefficients.

Overall, it can be said that for 15, 60 and 105 min of reaction time, the influence of the catalyst loadings is negligible and the results seem to be only dependent on hydrogen peroxide concentration in the modified AFP. However, it should be noted that the presence of iron metal catalyst is necessary for mineralization of phenol as preliminary experiments indicated that the combination of hydrodynamic cavitation and hydrogen peroxide (without iron metal catalyst) does not result in any TOC removal. Thus, even if catalyst loading does not play a significant role in deciding the extent of degradation, its presence in the system is equally important.

A change in the behaviour is observed in the 3D response surface at 15, 60 and 105 min. Maximum values of TOC conversions are seen with catalyst amounts ranging from medium to high (0–1) and at a hydrogen peroxide concentration of 2000 mg/L. For all the catalyst loadings employed, relative maximum values are obtained around this hydrogen peroxide concentration (2000 mg/L).

The amount of dissolved iron was determined at different concentrations of hydrogen peroxide. Fig. 7 shows the amount

of total dissolved iron in the solution after 105 min of phenol wastewater treatment by the combination of hydrodynamic cavitation and the AFP. Not surprisingly the more iron pieces present the greater the amount of iron that dissolves and

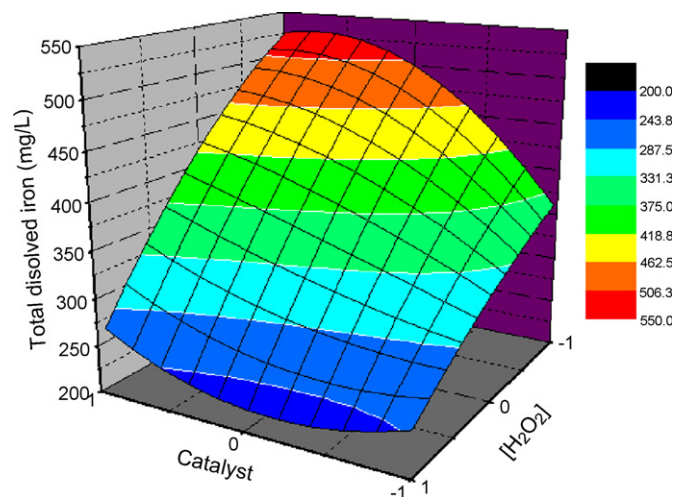


Fig. 7. The surface response curve of the total dissolved iron content after 105 min of treatment time.

maximum values are obtained with low concentrations of hydrogen peroxide. It should be pointed out that high concentration of hydrogen peroxide can retard corrosion of iron metal surfaces (passivation) as it can act as an electron donor at anodic sites [8] and this can explain why the lower iron content at higher concentration of hydrogen peroxide is observed.

Considering the coefficients of Eq. (7), the major influence corresponds to changes in the amount of iron metal pieces in the reaction medium ( $X$ ,  $X^2$ ). Only high levels of hydrogen peroxide ( $Y^2$ ) or the combination of hydrogen peroxide and catalyst ( $XY^2$  and  $YX^2$ ) have an appreciable influence in the degree of dissolution. In all these cases, an increase in the individual variable or in the combination of both of them results in an increase in the amount of iron in solution as shown by plus signs before the coefficients. The 3D response surface corresponding to Eq. (7) for the total dissolved iron content in the solution after 105 min of treatment time is shown in Fig. 7 and there is a strong correlation between catalyst loadings and the degree of iron dissolution. The amount of catalyst used at high concentration of hydrogen peroxide seems to have a negligible influence on the dissolved iron content, while at a lower concentration of hydrogen peroxide the response surface shows a relative maximum. Eq. (7) fits the experimental values, in terms of total iron dissolved in the solution.

#### 4. Conclusions

Zero valent iron is a promising catalyst for the treatment of phenolic aqueous solutions by the combination of hydrodynamic cavitation induced by the liquid whistle reactor with the AFP (modified AFP). Use of hydrodynamic cavitation enhances the efficacy of the AFP by keeping the iron surface active with the continuous impingement of the liquid jet stream flowing over the catalyst surface and at the same time providing additional free radicals for oxidation.

The current work has clearly shown that the modified AFP results in degradation of phenol and is indeed suitable for industrial wastewater applications. The efficacy of the treatment scheme is enhanced by high operating pressures, an increase in the oxidant dosage and a lowering of the pollutant concentration. The position of the catalyst bed with respect to the hydrodynamic cavitation unit is also important and it should be within the zone of influence of the cavities generated at the orifice.

The factorial design of experiments results in a removal of 50–60% TOC after 105 min of treatment time with the modified AFP with an optimal  $H_2O_2$  concentration of 2000 mg/L (high value) and with 50 pieces of iron catalyst (mid value). The hydrogen peroxide dosage plays a more vital role than the catalyst amount in the modified AFP.

Thus, the combination of hydrodynamic cavitation along with the advanced Fenton process offers a viable treatment scheme for industrial wastewater and the current work has described optimisation of the operating parameters with the aim of cost reduction by a combination of experimental and statistical analysis.

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